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Reuse of nickel recovered from spent Ni–Cd batteries for the preparation of C/Ni and C/Ni/Pd layered electrodes for energy sources

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A B S T R A C T

Nickel recovered in the recycling process of Ni–Cd batteries was used as a main component of bath for electrodeposition of nickel onto carbon fabric in order to obtain C/Ni composite. A part of the obtained composite was additionally coated with a thin layer of palladium (C/Ni/Pd composite). All the materials were investigated to assess the possibility of their use in the processes of electrochemical storage (sorption/desorption) of hydrogen and electrochemical oxidation of methanol. The obtained results showed the composites to be active electrode materials in these processes. The electrodes exhibited high activity and cyclability, especially in the process of methanol oxidation due to electrocatalytic activity of both nickel deposited onto carbon fabric and the outer layer of porous palladium coating nickel substrate.

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Keywords: Nickel–cadmium battery recycling; Carbon fabric; C/Ni electrode; C/Ni/Pd electrode; Hydrogen storage; Methanol oxidation

1. Introduction

The rapid development of electronics, electrical engineering and telecommunications causes an increasing need for small sources of electricity. Disposal of spent nickel–cadmium (Ni–Cd) batteries (Czerwiński and Rogulski, 2004; Rogulski and Czerwiński, 2006) is nowadays of prime importance due to their large number and simultaneous presence in high concentration of two different types of metals constituting the electrodes: extremely toxic cadmium and toxic nickel and cobalt. The utilization remains still important despite Ni–Cd batteries are increasingly replaced with nickel–metal hydride batteries (Ni–MH) (Köhler et al., 2004; Morioka et al., 2001) in which nickel and nickel hydroxides are invariably the main components of cathodes.

Recycling of spent batteries can be based on the recovery of metals in hydrometallurgical processes (Korsaga et al., 2006; Rącz and Ilea, 2013; Innocenzi and Veglio, 2012a,b; Santos

et al., 2012; Rogulski and Czerwiński, 2004) that are more favorable than pyrometallurgical ones (Espinosa and Tenório, 2004; Espinosa et al., 2004), due to the possibility of recovery of high purity metals without emission of pollutants to atmosphere and with low energy requirements (Korsaga et al., 2006; Rydh and Karlström, 2002).

It has been reported that cathode material separated from spent Ni–Cd batteries dissolves well in sulfuric acid (Bartolozzi et al., 1995; Nogueira and Margarido, 2004; Skowroński and Osińska, 2008), and the leach solutions contain nickel admixed with iron, cobalt, and cadmium. Many attempts to separate selectively metals from these solutions using solvent extraction have been made (Nogueira and Delmas, 1999; Reddy et al., 2006; Salgado et al., 2003; Skowroński and Osińska, 2009a). The recovery of these metals by extraction can be made from chloride acid solutions (Reddy et al., 2005; Sarangi et al., 1999). A solvent extraction of metals from sulfate solutions (Nogueira and Delmas, 1999; Salgado et al., 2003) has also been conducted using DEHPA and Cyanex 272 as extractants.

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The electrochemical technique allowing recovering metals from acid solutions was used by Freitas and Rosalém (2005), Rozário et al. (2006) and Yang (2003). Cadmium after leaching by sulfuric acid with addition of hydrogen peroxide can be recovered from spent Ni–Cd batteries using electrolysis (Bartolozzi et al., 1995; Freitas and Rosalém, 2005). The recovered cadmium was contaminated with 1.2 wt.% of nickel, whereas nickel remaining in solution was precipitated as carbonate containing less than 0.5 wt.% of cadmium. Because nickel hydroxide is an important active material applicable in alkaline batteries, different precipitation conditions were undertaken for its preparation (Osińska et al., 2003, 2004; Ramesh and Vishnu Kamath, 2006; Skowroński and Osińska, 2009b; Subbaiah et al., 2003; Yang, 2002).

The aim of this work was to study the possibility of use of nickel derived from recycling of nickel–cadmium batteries for the preparation of the new types of electrode materials based on porous carbon fabric carrier and to determine their electrochemical properties.

2. Experimental

2.1. Solutions and materials

Nickel sulphate recovered in the recycling process of Ni–Cd batteries (Skowroński and Osińska, 2008, 2009a) was used as a main component of Watt's type bath, applied commonly in the electrodeposition process. The electrolyte composed of NiSO_4 (80 g/dm³), $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ (50 g/dm³), $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (5 g/dm³) and $\text{H}_3\text{BO}_3 \cdot 10\text{H}_2\text{O}$ (20 g/dm³) was prepared for nickel electroplating.

Carbon fabric (sample C), prepared by the carbonization of PAN precursor, was used as the starting electrode carrier. Before nickel electrodeposition, the original carbon fabric was immersed in 1 M H_2SO_4 for 30 min to improve its wettability in bath. In the first step of the process, nickel was deposited from this solution onto carbon fabric for 5 h at a current density of 5 mA/cm². This process resulted in carbon fabric/nickel (C/Ni) composite. The amount of deposited nickel calculated from the weight difference of the electrode before and after the process of Ni deposition was equal to 30 mg/cm².

Subsequently, a part of obtained C/Ni composite electrodes was coated with a thin layer of palladium. Pd layer (1.3 mg/cm²) was deposited using chemical method by immersing C/Ni electrodes in aqueous solution of 0.11 M PdCl_2 in 1 M HCl (Skowroński et al., 2007). As a result of this process, a three layer carbon/nickel/palladium (C/Ni/Pd) composite electrode was prepared.

2.2. Sample characterization

A scanning electron microscopy (SEM) (Hitachi S-3400N) coupled with the energy dispersive spectrometer (EDS) (Thermo Electron Corp., model No. 4481B-1UES-SN with the NSS Spectral Imaging System software) was used for observing the morphology and surface distribution of active particles of samples as well as determining semi-quantitatively their chemical composition.

The characterization of the crystalline structure of pristine carbon fabric, carbon fabric covered with nickel and palladium layer deposited onto carbon fabric/nickel surface was carried out by the X-ray diffraction (XRD) measurements (Philips PW-1710 diffractometer) using $\text{CuK}\alpha$ radiation with nickel filtering.

2.3. Evaluation of electrochemical properties

The carbon carrier and carbon composite materials were investigated by the cyclic voltammetry (CV) method for evaluating the possibility of their use as electrode carriers for Ni–MH batteries as well as electrodes for both electrochemical hydrogen storage (sorption/desorption) and electrochemical oxidation of methanol. The CV measurements were carried out in a three-electrode cell. A Hg/HgO/6 M KOH system (−0.098 V vs. normal hydrogen electrode) and a platinum net were used as the reference and counter electrode, respectively. All potentials in the paper are related to Hg/HgO/6 M KOH reference electrode.

Hydrogen sorption/desorption process was examined in aqueous solution of 6 M KOH. Starting from the rest potential of electrode with a scan rate 10 mV s^{−1}, the potential was changed in the negative direction (cathodic polarization) and after the reversal of polarization the potential was increased until the limit potential was attained. At this moment the polarization was again reversed. The process of methanol oxidation was examined in 6 M KOH admixed with 1 M CH_3OH . In this case the CV measurements were carried out using a scan rate 50 mV s^{−1} starting from the rest potential of electrode in the positive direction. All electrochemical measurements were carried out at a room temperature using AUTOLAB potentiostat-galvanostat (model PGSTAT 30).

3. Results and discussion

3.1. SEM investigations

Fig. 1 shows SEM micrographs recorded for the original carbon fabric (a, b), nickel layer deposited on carbon fabric (c, d) and palladium layer coating nickel substrate (e, f). As can be seen in Fig. 1a and b, carbon fabric is built of plaited carbon fiber bundles. A thin and tight layer of nickel was produced as a result of nickel electrodeposition on the carbon fabric. Fig. 1c shows differences in morphology between the original carbon carrier and obtained C/Ni composite by presenting the interface between the carbon surface coated and uncoated with nickel of which the latter remained over the electrolyte level during the process of metallization. Fig. 1d recorded under a higher magnification shows that the electrodeposited layer of nickel is porous with numerous grains boundaries visible on the surface of nickel layer which can be assumed to be favorable for electrochemical activity.

As effect of subsequent coating the nickel/carbon composite with palladium, a porous deposit was formed onto the nickel surface (Fig. 1e and f). Spherical Pd grains ranging mostly from 0.5 to 1 μm in diameter are observed in Fig. 1f. Due to a short time of deposition the obtained Pd layer does not completely covers the Ni sublayer.

3.2. XRD and EDS measurements

Fig. 2 presents the XRD patterns recorded for the original carbon fabric (line a), carbon fabric covered with nickel (line b) and palladium layer deposited onto carbon fabric/nickel surface (line c). The lack of the diffraction peaks on the XRD pattern recorded for the original carbon fabric shows that the carbon material used as matrix has an amorphous structure. The XRD pattern obtained for Ni/C composite (line b) contains diffraction peaks corresponding only to metallic nickel

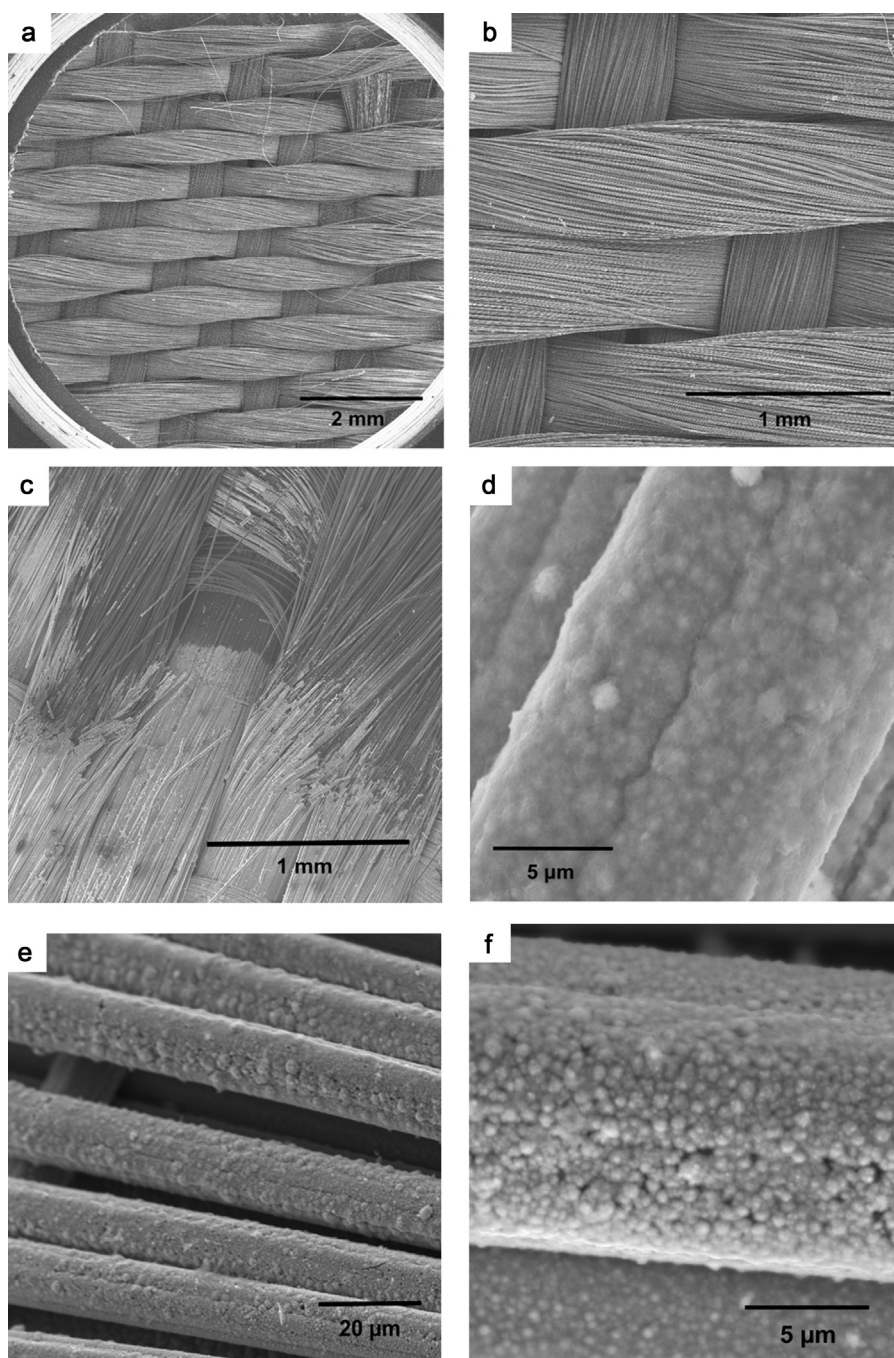


Fig. 1 – SEM images of the structure of carbon fabric (a, b), nickel deposited on carbon fabric (c, d), palladium catalyst deposited on the surface of nickel (e, f).

Ni (111), Ni (200) and Ni (200). This fact means that the other metals (Co, Fe, Cd) originating from spent Ni–Cd batteries were effectively removed from the leaching solution subsequently used as a nickel source. The procedure of chemical removing of Co, Fe and Cd has been described in our previous work (Skowroński and Osińska, 2009a). Upon coating the nickel surface with palladium (line c), the intensity of the diffraction peaks corresponding to metallic nickel decreased and the small diffraction peak assigned to metallic palladium Pd (111) occurs.

The results of the XRD and EDS analyses (Figs. 2 and 3) confirmed that the obtained three layered composite C/Ni/Pd contains only Ni and Pd particles. No other metals have been found in the metallic deposit. Additionally, EDS line scan analysis (Fig. 3b and c) performed along with fiber axis shows that the chemical surface composition of the obtained composite is

homogenous and the small variations visible on the recorded curves are connected only with the changes in surface morphology of the examined material.

3.3. The CV measurements in KOH in the potential range: $-1.1 \leftrightarrow 0.3$ V

Figs. 4–6 present cyclic voltammograms for electrodes C, C/Ni and C/Ni/Pd, respectively, recorded during cycles 3, 4 and 5 in the potential range from -1.1 to 0.3 V. On reaching the lower limit potential (-1.1 V) in cycle 4 the potential scanning was stopped for 15 min to proceed the potentiostatic sorption of hydrogen and then the potential run was continued in the positive direction to reach the high limit potential. As seen in Fig. 4, the potentiostatic sorption of hydrogen in carbon cloth resulted in the formation of broad, wide

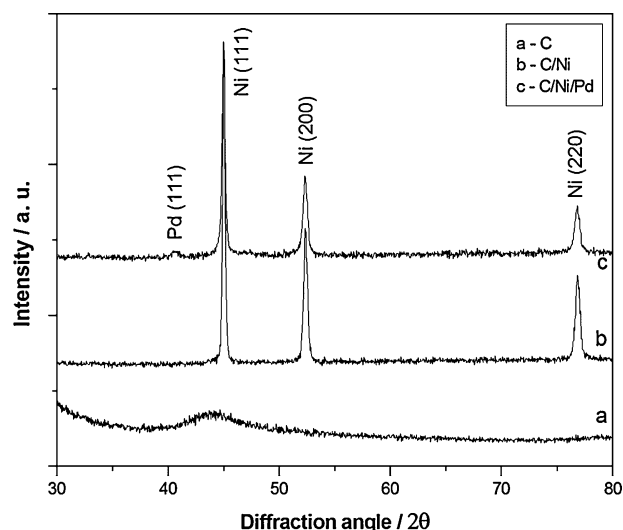


Fig. 2 – XRD pattern for pristine carbon fabric (line a), carbon fabric covered with nickel (line b) and palladium layer deposited onto carbon fabric/nickel surface (line c) using CuK α radiation.

and relatively flattened anodic peak with the maximum at around -0.6 V. In agreement with the results published previously (Skowroński et al., 2009) this peak is related to the oxidation reaction of hydrogen sorbed in carbon fibers during the potentiostatic polarization of electrode at -1.1 V. In the next cycle (without the potentiostatic polarization) the anodic peak corresponding to hydrogen oxidation (desorption)

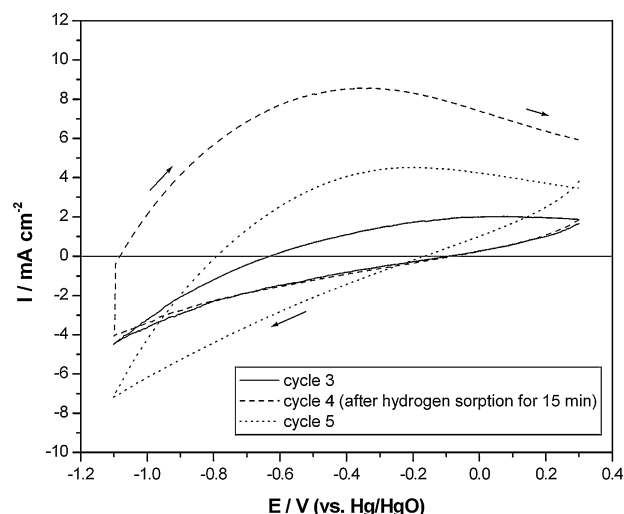


Fig. 4 – Cyclic voltammograms recorded in 6M KOH for carbon fabric electrode. Potential range: -1.1 V \leftrightarrow 0.3 V. Scan rate: 10 mV/s.

significantly decreases but still remains higher than that noted in cycle 3.

As seen in Fig. 5, the cathodic current densities recorded for carbon electrode coated with metallic nickel are significantly higher than those for uncoated carbon fabric due to electrocatalytic action of nickel in the process of hydrogen sorption/desorption. After the polarization direction is reversed at -1.1 V the anodic peak arising from both the desorption of hydrogen from the electrode material and

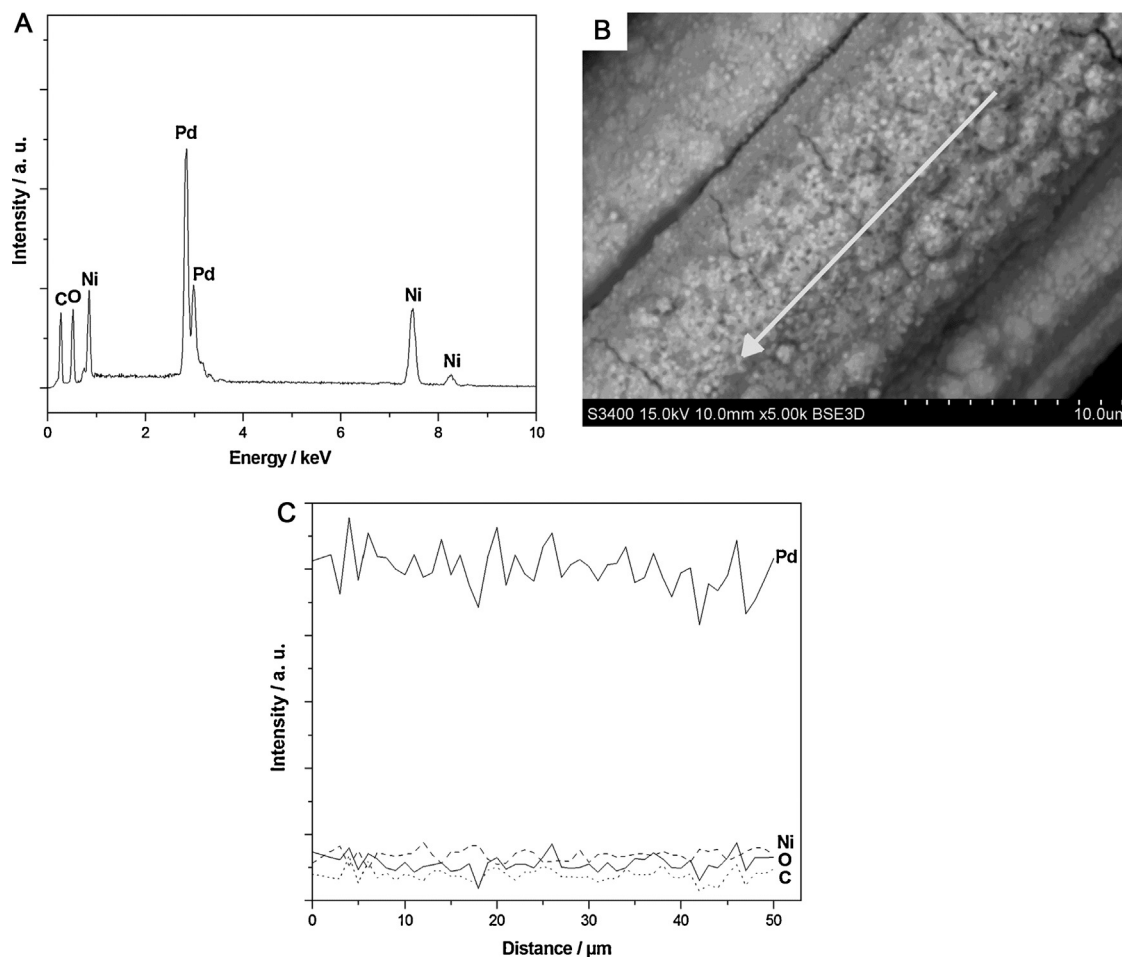


Fig. 3 – EDS analysis of the carbon fabric/nickel/palladium composite: (a) spectrum and (b, c) line scan.

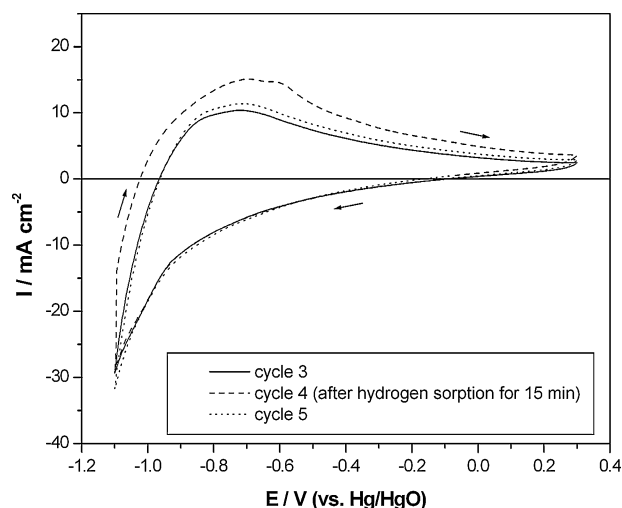


Fig. 5 – Cyclic voltammograms recorded in 6 M KOH for C/Ni electrode. Potential range: $-1.1 \text{ V} \leftrightarrow 0.3 \text{ V}$. Scan rate: 10 mV/s.

transformation of metallic nickel into $\text{Ni}(\text{OH})_2$ is recorded at -0.7 V (Skowroński et al., 2008; Skowroński and Rozmanowski, 2006). The effect of cathodic polarization of electrode C/Ni at the potential of hydrogen sorption (-1.1 V) in cycle 4 is observed as the increase in the amount of sorbed hydrogen simply related to the growth of the responding anodic peak at the potential of -0.7 V . During the next cycle (cycle 5), the peak intensity returns to that recorded in cycle 3 proceeded without the potentiostatic sorption of hydrogen. In contrast to a broad anodic peak noted for carbon electrode (Fig. 4), the peak of hydrogen desorption from electrode C/Ni is narrower and its maximum shifted to negative potentials (around -0.6 V) indicates that hydrogen can be recovered easier due to the reaction of hydrogen desorption occurring at a lower overpotential. Moreover, the anodic current densities recorded for electrode C/Ni in the potential region of hydrogen desorption are over twice higher than for carbon electrode.

In Fig. 6, CV curves recorded for electrode C/Ni/Pd are depicted. Their character is the same as those described in the literature for palladium limited volume electrodes (Pd-LVE) obtained by the deposition of a thin layer of palladium on gold (Czerwiński et al., 2000; Grdeń et al., 1999)

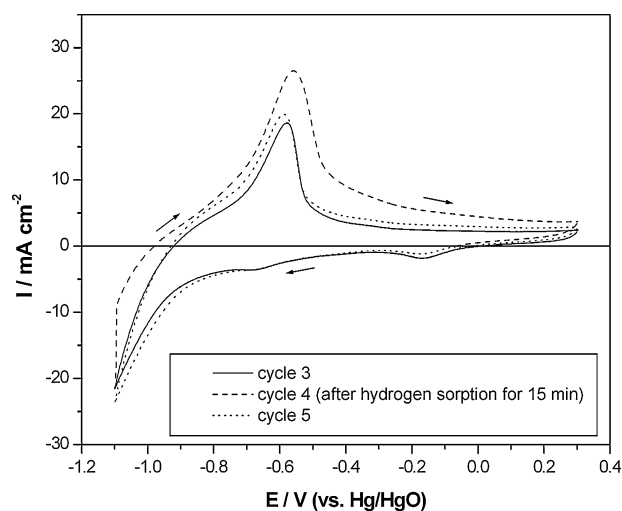


Fig. 6 – Cyclic voltammograms recorded in 6 M KOH for C/Ni/Pd electrode. Potential range: $-1.1 \text{ V} \leftrightarrow 0.3 \text{ V}$. Scan rate: 10 mV/s.

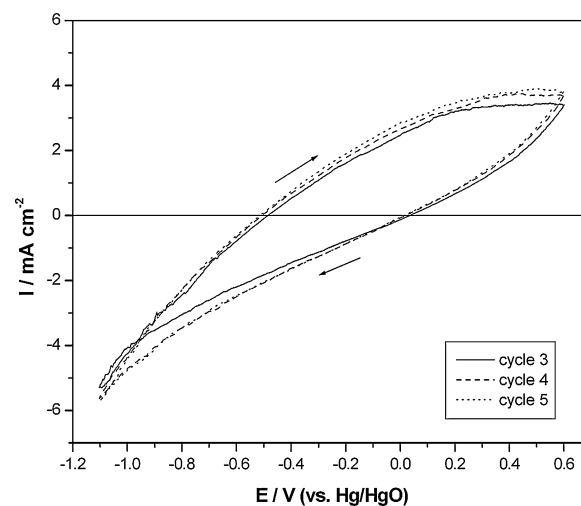


Fig. 7 – Cyclic voltammograms recorded in 6 M KOH for carbon fabric electrode. Potential range: $-1.1 \text{ V} \leftrightarrow 0.6 \text{ V}$. Scan rate: 10 mV/s.

and on nickel (Skowroński et al., 2009, 2007; Skowroński and Rozmanowski, 2013). A small cathodic peak at the potential of -0.7 V and increasing cathodic current noted during further scanning toward more negative potentials, are associated with hydrogen sorption on/in the examined electrode, whereas the anodic peak at -0.6 V corresponds to the oxidation reaction of hydrogen adsorbed/absorbed in electrode C/Ni/Pd (hydrogen desorption) (Skowroński et al., 2009, 2007) and the formation of $\alpha\text{-Ni}(\text{OH})_2$ (Skowroński et al., 2013, 2008). As the potential increases over -0.6 V the oxidation of Pd to Pd oxide occurs. After the reversal of polarization toward negative direction, palladium oxide is reduced within a small cathodic peak positioned at the potential of -0.2 V . Because this peak appears already in the first cycle (not shown in Fig. 6), one can infer that oxide layer was present on palladium surface before the beginning of electrochemical measurements. The potentiostatic polarization in cycle 4 at -1.1 V leads to the increase in the anodic peak localized at -0.55 V . This result can be attributed to enhanced amount of hydrogen recovered from the electrode. During the next cycle (cycle 5) without potentiostatic polarization at -1.1 V the charge of anodic peak of hydrogen sorption, likewise for C/Ni electrode (Fig. 5), returns to that noted in cycle 3 recorded without potentiostatic polarization. This means that an additional amount of hydrogen, sorbed in the electrode material during the potentiostatic sorption, is recovered only during the anodic run proceeding immediately after such a cathodic charging.

3.4. The CV measurements in KOH solution the potential range: $-1.1 \leftrightarrow 0.6 \text{ V}$

Figs. 7–9 depict cyclic voltammograms for C, C/Ni and C/Ni/Pd electrodes, respectively, recorded during cycles 3, 4 and 5 in the potential range from -1.1 to 0.6 V . On increasing the upper limit potential up to 0.6 V no significant change in the character of voltammetric curves is noted for carbon electrode (Fig. 7) as compared to the same electrode polarized up to 0.3 V (Fig. 5).

During the positive scan of electrode C/Ni in extended potential range the anodic peak, corresponding to the oxidation of $\text{Ni}(\text{OH})_2$ to $\beta, \gamma\text{-NiOOH}$ (Czerwiński et al., 1999; D'Alkaine and Santanna, 1998), appears at the potential of 0.55 V (Fig. 8). After the reversal of polarization to the negative direction (cathodic polarization) the cathodic peak

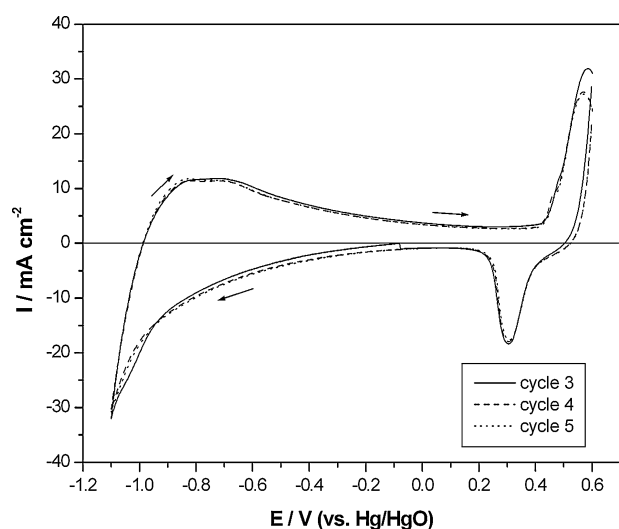


Fig. 8 – Cyclic voltammograms recorded in 6 M KOH for C/Ni electrode. Potential range: $-1.1\text{ V} \leftrightarrow 0.6\text{ V}$. Scan rate: 10 mV/s .

representing the reduction process $\beta,\gamma\text{-NiOOH} \rightarrow \beta\text{-Ni(OH)}_2$ is noted at 0.31 V . In subsequent cycles these effects are repeated indicating a high stability of electrode C/Ni in the redox reaction $\text{Ni(OH)}_2 \leftrightarrow \text{NiOOH}$ which gives the possibility of use of this type of electrode material as nickel cathodes in Ni–MH batteries. On the other hand, it is seen in Fig. 8 that the widening of the potential range to 0.6 V has no significant influence on the process of reversible hydrogen sorption as compared to Fig. 5.

Cyclic voltammograms obtained for a three-layer C/Ni/Pd electrode (Fig. 9) shows the increase of anodic current commencing from the potential of 0.5 V . This effect is attributed to the aforementioned reaction $\text{Ni(OH)}_2 \rightarrow \text{NiOOH}$ as well as to the overoxidation reaction resulting in oxygen evolution. After the reversal of polarization direction the cathodic peak corresponding to the reaction reduction of $\beta\text{-NiOOH}$ (0.31 V) is recorded (Czerwiński et al., 1999; D'Alkaine and Santanna, 1998). The presence of this couple of peaks arising from the reactions $\text{Ni(OH)}_2 \leftrightarrow \text{NiOOH}$ indicates that the Pd layer is porous and does not tightly cover the nickel layer. Due to permeability of Pd layer the three-layer C/Ni/Pd electrode exhibits combined activity characteristic of both Pd and Ni

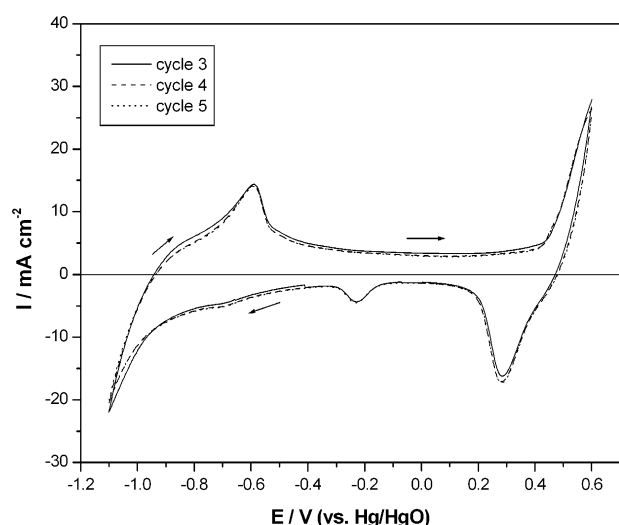


Fig. 9 – Cyclic voltammograms recorded in 6 M KOH for C/Ni/Pd electrode. Potential range: $-1.1\text{ V} \leftrightarrow 0.6\text{ V}$. Scan rate: 10 mV/s .

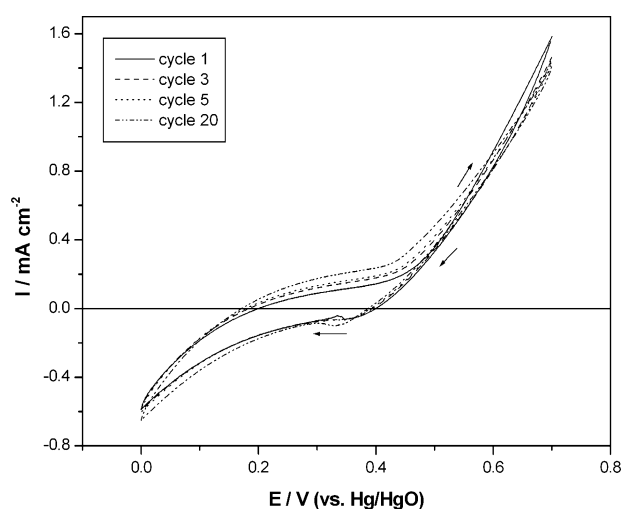


Fig. 10 – Cyclic voltammograms recorded for methanol oxidation on carbon fabric electrode in 6 M KOH containing $1\text{ M CH}_3\text{OH}$. Potential range: $0\text{ V} \leftrightarrow 0.7\text{ V}$. Scan rate: 50 mV/s .

electrode. In contrast to C/Ni electrode the shifting of the upper limit potential to 0.6 V leads to the decrease in the activity of C/Ni/Pd electrode in the region of the reaction of hydrogen sorption/desorption which is illustrated by lowering the anodic peak recorded at the potential of -0.6 V .

3.5. The CV measurements for methanol oxidation

CV curves recorded in KOH solution containing methanol are presented in Figs. 10–12.

The lack of anodic peak in Fig. 10 indicates that the reaction of methanol oxidation does not occur on carbon fabric electrode.

Cyclic voltammograms recorded in KOH solution admixed with CH_3OH for electrode C/Ni (Fig. 11) exhibit a significant increase of anodic current starting at the potential of 0.42 V and reaching the maximum value of 100 mA/cm^2 at 0.7 V . Because a sudden increase in current associated with the anodic oxidation of methanol takes place at the potential range corresponding to the oxidation of Ni(OH)_2 to NiOOH , the peak associated with the reaction of methanol oxidation is hidden from view. The overlapping of the two reactions agrees

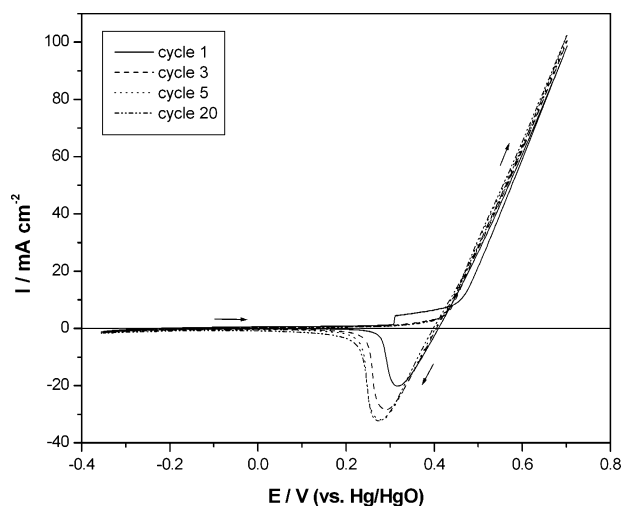


Fig. 11 – Cyclic voltammograms recorded for methanol oxidation on C/Ni electrode in 6 M KOH containing $1\text{ M CH}_3\text{OH}$. Potential range: $-0.35\text{ V} \leftrightarrow 0.7\text{ V}$. Scan rate: 50 mV/s .

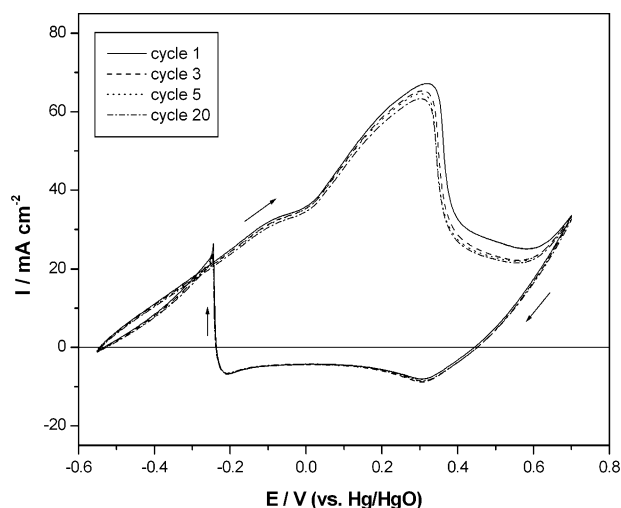


Fig. 12 – Cyclic voltammograms recorded for methanol oxidation on C/Ni/Pd electrode in 6 M KOH containing 1 M CH₃OH. Potential range: $-0.55\text{ V} \leftrightarrow 0.7\text{ V}$. Scan rate: 50 mV/s.

with the mechanism of methanol oxidation over nickel catalyst. According to this mechanism the reaction of methanol electrooxidation is catalyzed by Ni(III) ions simultaneously formed on the surface of C/Ni electrode in the reaction $\text{Ni}(\text{OH})_2 \rightarrow \text{NiOOH}$ (Rahim Abdel et al., 2004; Skowroński and Ważny, 2005, 2006). Although from thermodynamic point of view in this potential range the anodic evolution of oxygen might also be expected, no evolution of gas from the electrode was observed during measurement. The reason for such a behavior can be attributed to a high overpotential of oxygen evolution caused by methanol molecules as well as intermediate products of its oxidation adsorbed on the electrode surface (Skowroński and Ważny, 2006). The cathodic peak observed at 0.3 V after the reversal of polarization direction is indicative of the $\text{NiOOH} \rightarrow \text{Ni}(\text{OH})_2$ reaction.

The electrochemical oxidation of methanol on C/Ni/Pd electrode is a proof of simultaneous catalytic action of Ni and Pd coating on the surface of carbon fabric (Fig. 12). Besides the increase in anodic current density in the potential range from 0.6 to 0.7 V resulting from methanol oxidation on Ni catalyst, on the recorded CV curves a huge anodic peak arising from the oxidation of methanol on the Pd catalyst is recorded at 0.32 V. A pre-peak seen at the potential of -0.1 V on its left shoulder can be attributed to the synergistic effects of Ni and Pd in the methanol oxidation, while the main peak, with the maximum at the potential of 0.3 V, corresponds to the reaction of methanol oxidation on Pd (Singh et al., 2009; Skowroński and Rozmanowski, 2013; Xu et al., 2008). The anodic peak jump appearing at -0.25 V during the backward scanning is characteristic of the reactivation of electrode surface (Singh et al., 2009). It is noteworthy that a high activity of composite electrode C/Ni/Pd in the process of methanol electrooxidation remains almost unchanged on cycling.

4. Conclusions

Nickel recovered in the recycling process of Ni–Cd batteries can be successfully used to synthesize a new type of layered electrode materials in the form of carbon fabric/nickel and carbon fabric/nickel/palladium composites potentially applicable for hydrogen storage and methanol oxidation. A SEM analysis revealed that nickel deposited on carbon fabric forms a porous and uniformly dense coating. The performed XRD and EDS

analysis showed that the layer of the deposited nickel does not contain metals like Co, Fe, Cd originating from Ni–Cd spent batteries. This fact means that they were effectively removed from the leaching solution subsequently used as a nickel source. The synthesized light and flexible C/Ni composite was tested to assess its usefulness as electrode material in the reversible reaction of $\text{Ni}(\text{OH})_2 \leftrightarrow \text{NiOOH}$ occurring in Ni–Cd and Ni–MH batteries. The results of the cyclic voltammetry measurements showed that as prepared electrode exhibits good performance and stability in this process. Furthermore, the obtained C/Ni composite electrode exhibited an electrochemical activity in the process of hydrogen sorption/desorption.

Separate electrochemical experiments were performed for a three-layer C/Ni/Pd composite electrode prepared by chemical deposition of palladium on nickel-coated carbon fabric. The CV measurements showed that composite C/Ni/Pd electrode with a thin layer of palladium represents a high activity and reversibility in both the process of electrochemical storage of hydrogen and electrochemical oxidation of methanol. It was shown that the C/Ni/Pd electrode can be markedly enriched with hydrogen owing to potentiostatic charging at the potential of -1.1 V .

The obtained results showed that nickel recovered from spent Ni–Cd batteries could be applied for the preparation of both cathode materials for Ni–Cd and Ni–MH batteries and anode materials for Ni–MH batteries and direct methanol fuel cells. The combination of low metal content in the electrodes with their high activity may contribute to the decrease of the environment pollution and advantageous energy conversion and storage. According to the best of our knowledge there is no information available about the research on the use of recycled nickel as potential electrode material in mentioned systems.

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